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(54) ADSORBENT FOR OXYGEN PSA(PRESSURE SWING ADSORPTION), ITS PREPARATION AND PREPARATION OF OXYGEN USING IT

(57)Abstract:
PROBLEM TO BE SOLVED: To improve selective adsorptivity of nitrogen by a method wherein a crystalline zeolite X with a specified molar ratio is used and lithium cation and cesium cation each with a specified amt. are incorporated in a crystalline zeolite X adsorbent being ion-exchanged with lithium cation.
SOLUTION: In preparing a zeolite adsorbent used for preparing oxygen gas, a crystalline zeolite X with a molar ratio of SiO2/Al2O3 of not larger than 3.0 is used and at least 90% cations associated with its Al2O3 tetrahedron unit are ion-exchanged. Thereafter, ion exchange is performed again with a mixed salt aqueous soln. wherein sodium cation is an essential cation and either monovalent cation of cesium cation or rubidium cation and/or a mixed cation thereof are incorporated with at least 1% and less than 5%. In addition, after lithium cation associated with Al2O3 tetrahedron unit is made to be at least 80% and less than 88%, it is washed, dried and activated.

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CLAIMS

[Claim(s)]
[Claim 1] the crystalline zeolite X which has from 3.0 the SiO2/aluminum2O3 mole ratio which is not size -- it is -- in addition -- and the crystalline zeolite X adsorbent one of whose cations and/or these mixed cations of a caesium cation, a rubidium cation, a potassium cation, a thallium cation, and a silver cation the lithium cations which are meeting per AlO2 tetrahedron are less than 88% 80% or more of all cations, and are less than 5% more than per %
[Claim 2] a crystalline zeolite X adsorbent according to claim 1 -- setting -- cation-exchange site III of the crystalline zeolite X l whose located lithium cations are less than 20% 10% or more of all cations -- crystalline zeolite X adsorbent characterized by things
[Claim 3] After carrying out the ion exchange of the 90% or more of the thione which is meeting per AlO2 tetrahedron of the crystalline zeolite X which has from 3.0 the SiO2/aluminum2O3 mole ratio which is not size by the lithium cation, A sodium cation is made into an indispensable cation. A caesium cation, a rubidium cation, The re-ion exchange is carried out in the mixed-salt solution containing one of the monovalent cations and/or these mixed cations of a potassium cation, a thallium cation, and a silver cation. How to manufacture the claim 1 characterized by being washed, dried and activated after making into less than 88% the lithium cation which is meeting per AlO2 tetrahedron 80% or more, and a crystalline zeolite X adsorbent according to claim 2.
[Claim 4] The manufacturing method of the crystalline zeolite X adsorbent which the total cation concentration of the mixed-salt solution concerned is 0.1Ns or less, carries out the re-ion exchange within [in the temperature of 60 degrees C or less, and 5 hours], and is characterized by being washed, dried and activated in the manufacture method of a crystalline zeolite X adsorbent according to claim 3 after making into less than 88% the lithium cation which is meeting per AlO2 tetrahedron 80% or more.
[Claim 5] The air separation method by pressure rocking adsorption which the nitrogen in air is made to stick to this adsorbent alternatively, and carries out separation recovery of the oxygen using a crystalline zeolite X adsorbent according to claim 1 or 2.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the adsorbent used in order to carry out separation recovery of the oxygen from air by pressure rocking adsorption (called PSA Pressure Swing Adsorption for short), its process, and the air separation method using it.
[0002] Oxygen gas is one of the most important gas also in industrial gas, and is widely used focusing on iron manufacture, pulp bleaching, etc.
[0003] If it continues till recent years, in fields, such as dust incineration and glass melting, oxygen-enrichment combustion is beginning to be adopted for the purpose of NOx generating reduction, and the importance of oxygen gas is increasing increasingly also from the position of earth environment protection.
[0004] Although there are the PSA method, a membrane-separation method, low temperature processing, etc. in the manufacture method of oxygen gas, recently, the ratio of the PSA method high-concentration oxygen gas is obtained by the low cost is increasing every year.
[0005]
[Description of the Prior Art] The zeolite adsorbent which adsorbs nitrogen gas alternatively was used for oxygen gas manufacture by the PSA method, and the adsorbent of the crystalline zeolites X and A which mainly carried out the ion exchange by the calcium cation has been used for it until now.
[0006] On the other hand, the crystalline zeolite X which carried out the ion exchange by the lithium cation in U.S. JP,3140933,B has become well-known [excelling in the separation property of air], and the adsorbent of the lithium exchange crystallinity zeolite X is recently improved. In U.S. JP,3140933,B, it is shown that the crystalline zeolite X is so highly efficient that the rate of lithium exchange is high, and the fact is reconfirmed in JP,5-25527,B and U.S. JP,5268023,B.
[0007] The lithium exchange crystallinity zeolite X is obtained by carrying out the ion exchange of the crystalline zeolite X using the solution containing lithium salt. However, since the lithium which is a rare metal was expensive, the crystalline zeolite X adsorbent with the high rate of lithium exchange became very expensive.
[0008] On the other hand, in addition to the lithium cation, 15% - 30% of alkaline-earth cation is mixed substantially, and the mixed cation-exchange zeolite X adsorbent which reduced the ratio of an expensive lithium cation is also proposed 5% or more (others [No. / 5152813 / U.S. JP,5174979,B and]).
[0009] However, although the amount of adsorption of nitrogen was large, the coadsorption of oxygen was also large and the performance as an adsorbent for air separation was [the selective-adsorption nature of nitrogen] inadequate [the crystalline zeolite X containing 5% or more of alkaline-earth cation] for the low reason as a result.
[0010]
[Problem(s) to be Solved by the Invention] Although the crystalline zeolite X adsorbent which carried out the ion exchange by the lithium cation had the outstanding selective-adsorption property of nitrogen,

it had become what has it in the adsorbent with the high rate of lithium exchange. [remarkable the oxygen gas cost manufactured using adsorbent cost and such an adsorbent and high]
[0011] then, the content of an expensive lithium -- as much as possible -- low -- stopping -- in addition -- and development of the adsorbent excellent in the cost performance which is excellent in the selective-adsorption nature of nitrogen was desired strongly
[0012]
[Means for Solving the Problem] As a result of a lithium cation's examining in detail the crystalline zeolite X adsorbent which carried out the ion exchange, even if a lithium cation is less than 88%, this invention person etc. A high air separation performance is obtained by carrying out the ion exchange in the mixed monovalent cation solution which has a difference in the free energy in the ion exchange. Site III which is an ion-exchange site which carries out a role important for adsorption of nitrogen by carrying out the ion exchange especially of the crystalline zeolite X until a lithium cation becomes 90% or more by the meeting ratio of an AlO2 tetrahedron unit first After introducing a lithium cation, A sodium cation is made into an indispensable cation. A caesium cation, a rubidium cation, By re-exchanging in the mixed-salt solution containing one of the monovalent cations and/or these mixed cations of a potassium cation, a thallium cation, and a silver cation It finds out that the performance which was excellent especially by sampling the lithium cation of the site I which is an ion-exchange site which does not participate in nitrogen adsorption capacity, and Site II is obtained, and comes to complete this invention. It is possible for the adsorbent of this invention to have few contents of an expensive lithium, to end, and to offer a highly efficient adsorbent more cheaply.
[0013] Below, this invention is explained in detail.
[0014] The mother zeolite crystal of the adsorbent used by this invention is the crystalline zeolite X which has the SiO2/aluminum2O3 mole ratio which is not size, and it is especially more desirable than 3.0 that SiO2/aluminum2O3 mole ratio is the crystalline zeolite X of 1.8-2.5.
[0015] The crystalline zeolite X is classified into a faujasite type (it is written as a henceforth FAU type) in crystallography, and is expressed with the following chemical formulas.
[0016] Mn O-aluminum2 O3, mSiO2, and lH2 O (the cation of m=2-3 and M:2/n **, l=0-8)
Why the zeolite kind of an adsorbent must be the crystalline zeolite X here is explained.
[0017] the static adsorption of the nitrogen to a zeolite and oxygen is physical adsorption, and according especially to the polarity (quadrupole child) of nitrogen and oxygen -- **** adsorption is the main adsorption driving force since nitrogen has the high quadrupole child moment compared with oxygen -- the adsorption to a zeolite -- a static -- if it is only **** attraction, high selectivity is obtained compared with oxygen adsorption, and nitrogen adsorption can expect a high value to the selectivity (here, it is expressed as a separation factor) of the nitrogen defined as relative volatility, and oxygen
[0018] On the other hand, nitrogen and oxygen are adsorbed by dispersion force (intermolecular force) to a zeolite. Since the adsorption by dispersion force does not have the selectivity of nitrogen adsorption and oxygen adsorption regardless of the polarity of an admolecule, a separation factor approaches 1. The influence of dispersion force becomes large, so that the adsorption space in a zeolite is small, since dispersion force is the interaction of a zeolite crystal and an admolecule, and the selectivity of nitrogen adsorption and oxygen adsorption falls.
[0019] Therefore, in order to raise the selectivity of nitrogen adsorption, the adsorption space of a mother zeolite crystal must be large, and it is the zeolite kind with which the crystalline zeolite X with large pore fitted air separation most.
[0020] On the other hand, it is known that the crystalline zeolite Y belongs to the FAU same in crystallography as the crystalline zeolite X. However, the crystalline zeolite Y is the ion-exchange site III important for nitrogen adsorption. Since a lithium cation has the specific property in which it is not exchanged, it cannot use for the mother zeolite of this invention.
[0021] Next, the mother zeolite crystal of the adsorbent used by this invention explains the reason which must be the crystalline zeolite X which has from 3.0 SiO2 / aluminum2O3 mole ratio which is not size.
[0022] Or more by three, SiO2 / aluminum2O3 mole ratio cannot be set to Y, and cannot use a zeolite for the reason explained previously.

[0023] Since the electrostatic attraction of a zeolite is formed of the exchange cation of a zeolite, more ones are [the number of cations] desirable. Although the amount of charge divalent may exist to AlO2 tetrahedron of a zeolite, the adsorption site of the cation of a zeolite increases as a zeolite with AlO2 high ratio per unit weight, i.e., the small zeolite of SiO2 / aluminum2O3 ratio.
[0024] In 1.8-2.5 with small SiO2/aluminum2O3 mole ratio, although, as for the crystalline zeolite X, SiO2/aluminum2O3 mole ratio can take less than three, in this invention, a high performance is obtained especially.
[0025] It is especially desirable that it is [whose small crystalline zeolite X of SiO2/aluminum2O3 ratio with the micropore large / the mother zeolite crystal of the adsorbent of the above reason to this invention / and under crystal, i.e., SiO2/aluminum2O3 mole ratio, is not size from 3] the crystalline zeolite X of 1.8-2.5.
[0026] Next, the rate of the ion exchange of the adsorbent of this invention is explained.
[0027] As for the ratio of a lithium cation, it is desirable that the lithium cations to which the adsorbent of this invention is meeting per AlO2 tetrahedron are less than 88% 80% or more of all cations, and are especially less than 88% 85% or more.
[0028] Since the lithium is especially expensive at 90% or more and the final rate of lithium exchange of this invention becomes [adsorbent cost] high 88% or more, it is not desirable. On the other hand, the rate of lithium exchange is the target ion-exchange site III at less than 80%. Since sufficient lithium cation cannot remain, it is not desirable.
[0029] Although the adsorbent of this invention contains one of the monovalent cations and/or these mixed cations of a caesium cation, a rubidium cation, a potassium cation, a thallium cation, and a silver cation as cations other than a lithium, especially the content of these monovalent cations has 2 to 4% of desirable range less than 5% more than per %. The content of these monovalent cations is Site III at 5% or more. Li cannot be maintained 10% or more, but an air separation property decreases remarkably. A cation's existence position (site) is explained in full detail behind. Cations other than a lithium cation and these monovalent cations are sodium cations.
[0030] The adsorbent of this invention is the cation-exchange site III of a crystalline X type zeolite. The located lithium cation is less than 20% 10% or more.
[0031] It is known well that three ion-exchange sites (Site I, Site II, and Site III are called) exist in the crystalline zeolite X. The site position of the crystalline zeolite X was shown in drawing 1 .
[0032] The cation located in an ion-exchange site forms an electrostatic field around it, and adsorbs a polar substance. Site III Since the located lithium cation exists in a crystal front face naked and can form a strong electrostatic field, it is a site convenient for nitrogen adsorption.
[0033] With the conventional ion-exchange technology, a lithium cation will be altogether located in the site I whose lithium cation is a stable site thermodynamically in less than 80% of all cations, and Site II. Therefore, at 80% or less, nitrogen adsorption capacity has a low rate of lithium exchange, and, for the rate of exchange, a lithium cation is Site III for the first time at 80% or more. It was located, and nitrogen adsorptivity ability was improving as the rate of exchange became high.
[0034] With the adsorbent of this invention, although the rate of a lithium cation exchange is low, it is the exchange site III of Zeolite X. By making the existing effective lithium cation into 10% or more, the selective-adsorption performance of nitrogen equivalent to the case where the rate of exchange is 90% or more can be demonstrated. On the other hand, it is the site III of the crystalline zeolite X. The cation which may exist is to 20% of all cations, and it is Site III about 20% or more of lithium cation. It is impossible for you to make it located.
[0035] It can ask for the ratio of the lithium cation of the crystalline zeolite X correctly by chemical analyses (ICP etc.). Ion-exchange site III Although it can ask for the ratio of the existing lithium cation also in X ray crystal structure analysis or neutron-beam analysis, it can be estimated from the adsorption property of nitrogen simpler.
[0036] For the lithium exchange crystallinity zeolite X by the conventional ion-exchange method, the rate of a lithium cation exchange is 80% to the exchange site III. Since it begins to be located, the rate of lithium exchange is Site III with 80% or more of crystalline zeolite X. The lithium cation and nitrogen

adsorptivity ability which are located are in proportionality, and it is the rate of lithium exchange and Site III of the crystalline zeolite X. The ratio of the existing lithium can be estimated from a nitrogen adsorption property (the nitrogen amount of adsorption
[0037] Next, the manufacture method of the crystalline zeolite X adsorbent of this invention is explained.
[0038] Although the mother zeolite crystal used by this invention is the crystalline zeolite X which has from 3.0 SiO2 / aluminum2O3 mole ratio which is not size, especially the manufacture method of the crystalline zeolite X is not limited, but can be compounded by the well-known method. For example, the manufacture method of the crystalline zeolite X with small SiO2/aluminum2O3 mole ratio is indicated by U.S. JP,2882244,B etc.
[0039] Although the adsorbent of this invention may also contain a binder, what zeolite-ized the binder component (binder loess) may be used. A binder kind is not limited but can illustrate a silica binder, an alumina binder, an aluminum silicate binder, a clay binder, etc. Since a binder does not have adsorptivity ability, the ratio of a binder has a few desirable thing.
[0040] The size of the adsorbent of this invention and a configuration are not limited, either, for example, the bead configuration and the pellet configuration where a path is 1.0-2.0mm can be illustrated.
[0041] The adsorbent of this invention carries out the ion exchange of the above-mentioned crystalline zeolite X 90% or more by the lithium cation, and is III of the ion-exchange site of the crystalline zeolite X. It is desirable to fully exchange a lithium cation. As for especially the rate of exchange of the lithium cation in this stage, it is desirable that all cations are 95% to 100% 90% or more.
[0042] Although especially the ion-exchange method is not limited, the method of making the lithium salt solution (for example, lithium-chloride solution) which adjusted the crystalline zeolite X to pH 10-11 by the lithium hydroxide, for example contacting can be illustrated. Although a batch type or a circulation formula is sufficient as the ion exchange, the ion exchange of a circulation formula is efficient. Although especially the temperature of the ion exchange is not limited, either, the higher one of temperature is especially efficient and it is desirable to carry out at 60 degrees C - 90 degrees C 40 degrees C - 100 degrees C.
[0043] By this invention, the re-ion exchange of the lithium cation of the exchange site I and Site II which does not participate in adsorption of nitrogen is carried out by other cations from the crystalline zeolite X which fully carried out the ion exchange by the lithium cation.
[0044] A part of rank of the free energy of a cation exchange was illustrated to drawing 2 . Since the state of the sodium cation which is a start raw material served as criteria, the energy level of a sodium type zeolite was set to 0.
[0045] **G from a sodium cation to a caesium cation, a rubidium cation, a potassium cation, a thallium cation, and a silver cation which carries out the ion exchange is a negative value, and a reaction tends to progress so that this drawing 2 may show.
[0046] On the other hand, **G of the ion exchange from a sodium cation to a lithium cation is a positive value, a reaction cannot occur easily, and **G of the ion exchange is Site I, Site II, and Site III further. It becomes large and is hard to exchange in order of the site III > site II> site I in order. In the ion exchange in a lithium, it is called for from an ion-exchange-equilibrium constant in order of the site III > site II> site I that **G is large.
[0047] By this invention, the re-ion exchange of the lithium cation of the exchange site I and Site II which does not participate in adsorption of nitrogen is carried out by other cations from the crystalline zeolite X which fully carried out the ion exchange by the lithium cation. However, it is Site III if the crystalline zeolite X which carried out the ion exchange by the lithium cation is re-exchanged with sodium cation independent ion-exchange liquid. Site III which is a cation important for nitrogen adsorption since exchange of a lithium cation has negative biggest **G The ion exchange of the lithium cation will be carried out preferentially.
[0048] this invention person etc. here A sodium cation, a caesium cation, a rubidium cation, A potassium cation, a thallium cation, It sets to re-exchange of the mixed ion-exchange solution containing

h g cg b eb cg e e

one of the monovalent cations and/or these mixed cations of a silver cation, and is Site III. The lithium cation of Site I and Site II rather than the ion exchange of the lithium cation is carried out to a sodium cation Caesium cation, The direction of **G which carries out the ion exchange to the monovalent cation of a rubidium cation, a potassium cation, a thallium cation, or a silver cation finds out a large thing. A sodium cation, a caesium cation, a rubidium cation, a potassium cation, In the re-ion exchange of the mixed-salt system of the cation containing one of the monovalent cations and/or these mixed cations of a thallium cation and a silver cation, it found out that the lithium cation of Site I and Site II could be sampled.

[0049] The ion-exchange solution used for the re-ion exchange by this invention must contain both the monovalent cations of a sodium cation, a caesium cation and a rubidium cation, a potassium cation, a thallium cation, or a silver cation, and/or these mixed cations.

[0050] The amount of the monovalent cations of a caesium cation, a rubidium cation, a potassium cation, a thallium cation, or a silver cation and/or these mixed cations used must be less than 5% of all the exchange cations of the crystalline zeolite X after the re-ion exchange was carried out, and 2 to 4% of its range is especially desirable. The selective-adsorption performance of nitrogen is spoiled for these monovalent cations by 5% or more of all the exchange cations of the crystalline zeolite X.

[0051] As for the concentration of the ion-exchange liquid which carries out the re-ion exchange in the ion exchange of this invention, it is desirable that it is 0.1Ns or less and is especially 0.01Ns or less. the ionic strength of re-ion-exchange liquid -- being strong (that is, concentration being high) -- large site III of **G Since the reaction from which a lithium cation escapes becomes easy to advance, it is not desirable.

[0052] Moreover, what is necessary is just to also carry out re-ion-exchange temperature at a room temperature (25 degrees C) for a reason same as the above to the method of a low to be desirable, it be desirable to carry out below 60 degrees C, and for it be convenient.

[0053] Moreover, re-ion-exchange time has the shorter desirable one. If re-swap time is long, an ion-exchange site shifts to a state stable in energy, and it is Site III. A lithium cation will re-exchange for Site I and Site II. Especially re-ion-exchange time has less than 2 desirable hours for less than 5 hours.

[0054] The lithium collected from Site I and Site II by the ion exchange treatment of the adsorbent of this invention carries out separation recovery with the ion exchange, chemistry settling, etc., and can be reused effectively. recovery of a lithium cation, and the reuse method -- various kinds -- the method is not limited although well-known technique is applicable

[0055] Next, after the above-mentioned ion exchange, the adsorbent of this invention performs washing, dryness, and heat treatment (activation), and they are used for it as a target adsorbent for the first time.

[0056] Although washing, dryness, and especially activation conditions are not limited, it can illustrate that washing uses pure water or the water which adjusted pH to weak alkali by the lithium hydroxide of a minute amount.

[0057] It is desirable that performing dryness at low temperature performs 100 degrees C at 30 degrees C - 60 degrees C especially from a room temperature preferably.

[0058] It is desirable to perform it in the state of the low of a low-temperature steam partial pressure if possible, although activation is processing which removes the moisture which is sticking to the crystalline zeolite X by heating. For example, heat treatment of the inner heat type which supplies the vacuum heat-treatment in 300 degrees C - 600 degrees C, heated air, pure nitrogen or pure oxygen of a low dew-point among a vacuum can be illustrated.

[0059] Since the lithium cation to which the crystalline zeolite X adsorbent of this invention is meeting to AlO2 tetrahedron is less than 88%, the lithium cation which is meeting to AlO2 tetrahedron proposed previously differs from 88% or more of adsorbent (U.S. JP,4859217,B, JP,5-25527,B).

[0060] The alkaline-earth-metal cation by which the conventional proposal of the crystalline zeolite X adsorbent of this invention was made, not using an alkaline-earth-metal cation at all completely differs from 5% or more of crystalline zeolite X adsorbent (others [No. / 5152813 / U.S. JP,5174979,B and]).

[0061] Since elements other than a lithium are monovalent cations, the crystalline zeolite X adsorbent of this invention differs from the previous report patent (JP,8-4707,B, JP,7-256094,A) which has proposed

adding a bivalent or trivalent cation.

[0062] For the total rate of exchange of a lithium cation, the adsorbent of this invention is Site III with the method of U.S. JP,5268023,B, although U.S. JP,5268023,B is overlapped. Since it can enter only to 8% at the maximum, a lithium cation is Site III. As for the adsorbent of 10% or more of this invention, a lithium cation differs from the adsorbent of U.S. JP,5268023,B.

[0063] Since the adsorbent of this invention has the outstanding selective-adsorption ability of nitrogen, it makes nitrogen adsorb alternatively from air, and has the performance which was extremely excellent as an adsorbent used for the pressure rocking adsorption process (the PSA method) which obtains oxygen gas as a product.

[0064] The pressure rocking adsorption process (the PSA method) as used in the field of this invention makes the nitrogen in air adsorb alternatively, fluctuating a pressure, if it is the oxygen PSA method for obtaining oxygen gas as a product, especially limitation will not have it in the service condition, and they are 3 and the thing which the PSA method of a type, the VSA method, the VPSA method, etc. do not depend on the operation pressure range of rocking adsorption, but can demonstrate a high performance 2 column from a type 4 column.

[0065]

[Example] Next, although a concrete example explains this invention, this invention is not limited to these examples.

[0066] First, using the 1-N lithium chloride (it adjusts to pH-11 by the lithium hydroxide), the rate of lithium exchange was made into 95%, and pure water washed the example 1 - 10 crystallinity zeolite X. next, salt concentration -- sodium 0.01Ns or less, a rubidium, caesium and a thallium, silver, and the mixed-salt ghost solution of a potassium -- using -- a room temperature (25 degrees C) -- the re-ion exchange was carried out for 1 hour It dried at 40 degrees C after washing with pure water overnight, and the crystalline zeolite X which carried out the re-ion exchange was activated by the 350-degree C vacua for 1 hour. The pressure at the time of activation was performed by 5 or less torrs.

[0067] The separation factor (alpha) of SiO2 / aluminum2O3 mole ratio of the crystalline zeolite X which is a mother zeolite (Si/aluminum2), an Li/aluminum ratio, the rate of a cation exchange, the nitrogen amount of adsorption (QN2) in 700torr, and the air in nitrogen partial pressure 700torr was shown in Table 1, Table 2, and drawing 3 -6.

[0068]

[Table 1]

No.	Si/Al_2	Li/Al	カチオン交換率（%）							サイトIII Liカチオン率(%)	QN_2 (Ncc/g) at 10℃	α
			Li	Tl	Rb	Cs	Ag	K	Na			
実施例1	2.5	86	88	3	-	-	-	-	9	13±1	25.5	4.7±0.1
実施例2	2.5	86	88	-	2	-	-	-	10	13±1	25.3	4.6±0.1
実施例3	2.5	85	87	-	-	2	-	-	11	13±1	25.7	4.5±0.1
実施例4	2.5	85	87	-	-	-	3	-	10	13±1	24.8	4.6±0.1
実施例5	2.5	86	87	-	-	-	-	3	10	13±1	24.7	4.6±0.1
比較例1	2.5	86	87	-	-	-	-	-	13	7±1	19.0	4.1±0.1
比較例2	2.5	86	87	-	-	-	-	-	13	7±1	19.5	4.2±0.1

[0069]

[Table 2]

No.	Si/Al$_2$	Li/Al	ｶﾁｵﾝ交換率（%）							ｻｲﾄIII Liｶﾁｵﾝ率（%）	QN$_2$ (Ncc/g) at 10℃	α
			Li	Tl	Rb	Cs	Ag	K	Na			
実施例 6	2.0	86	88	2	-	-	-	-	9	13±1	27.5	5.7±0.1
実施例 7	2.0	86	88	-	2	-	-	-	10	13±1	27.3	5.6±0.1
実施例 8	2.0	85	87	-	-	2	-	-	11	13±1	27.0	5.5±0.1
実施例 9	2.0	85	87	-	-	-	2	-	10	13±1	27.8	5.6±0.1
実施例 1 0	2.0	86	87	-	-	-	-	3	10	13±1	27.4	5.6±0.1
比較例 3	2.0	86	87	-	-	-	-	-	13	7±1	20.5	5.0±0.1
比較例 4	2.0	86	87	-	-	-	-	-	13	7±1	21.0	5.1±0.1

[0070] The nitrogen partial pressure computed the separation factor (alpha : relative volatility) of the air in 700torr(s) by following several 1.
[0071]
[Equation 1]

$$\text{分離係数} = \frac{\text{窒素吸着量(at 700torr)}}{\text{酸素吸着量(at 700torr)}} \times \frac{\text{空気中の酸素濃度}}{\text{空気中の窒素濃度}}$$

[0072] The performance of Li exchange zeolite obtained with the conventional technology was also collectively shown in drawing 3 -6. By the method of this invention, the nitrogen amount of adsorption on the base of 80% with the rate of a lithium cation exchange higher than the case where the conventional technology is used, and the separation factor were obtained.
[0073] 90% of the weight, the with an example 11 - a 20 crystallinity zeolite X diameter [1.5mm diameter phi which consists of 10 % of the weight of kaolin binders as a binder] molding object was corned, and actual PSA operation was performed using the adsorbent which carried out the ion exchange so that it might become composition of examples 1-10.
[0074] as for PSA operation, an adsorption tower with a capacity of 2l. consists of two -- 2 columns were taken for the type and the adsorption cycle was made into double ** 30 seconds for desorption 30 seconds for adsorption 1 minute The pressure swing range was set to adsorptive pressure force 890torr (nitrogen partial pressure 700torr) and desorption pressure 180torr, and temperature of an adsorption tower was performed by two points, 0 degree C and 10 degrees C.
[0075] The result was shown in Table 3 and 4.
[0076]
[Table 3]

ＰＳＡ評価結果（Ｓｉ／Ａｌ₂＝２．５）

Ｎｏ．	組成	温度(℃)	酸素量(NL/kgh)	回収率(%)
実施例１１	実施例１と同等	0	82.0	57.0
		10	74.0	58.5
実施例１２	実施例２と同等	0	80.5	56.5
		10	72.5	57.5
実施例１３	実施例３と同等	0	82.5	56.0
		10	74.5	57.0
実施例１４	実施例４と同等	0	82.0	57.5
		10	74.0	56.5
実施例１５	実施例１と同５	0	82.5	57.5
		10	74.0	57.0
比較例５	比較例１と同等	0	75.0	50.5
		10	70.0	51.0
比較例６	比較例２と同等	0	76.5	51.0
		10	71.0	51.5

[0077]
[Table 4]

ＰＳＡ評価結果（Ｓｉ／Ａｌ$_2$＝２．０）

Ｎｏ．	組成	温度(℃)	酸素量(NL/kgh)	回収率(%)
実施例１６	実施例６と同等	0	106.5	65.0
		10	95.0	63.5
実施例１７	実施例７と同等	0	104.0	63.0
		10	93.5	62.0
実施例１８	実施例８と同等	0	106.0	64.0
		10	92.0	61.5
実施例１９	実施例９と同等	0	105.5	63.5
		10	93.0	61.5
実施例２０	実施例１０と同等	0	105.0	63.5
		10	92.5	61.0
比較例７	比較例３と同等	0	99.0	53.5
		10	88.0	53.0
比較例８	比較例４と同等	0	100.0	54.0
		10	90.0	53.5

[0078] The adsorbent of this invention showed the high performance also in actual PSA operation, and the high performance was demonstrated also in the low-temperature property (0 degree C) which poses a problem especially in a real plant.
[0079] The rate of lithium exchange was first made into 87% and 95% for the example 1 of comparison - 4 crystallinity zeolite X using the 1-N lithium chloride (it adjusts to pH-11 by the lithium hydroxide). the Plastic solid of 95% of rates of lithium exchange -- salt concentration -- sodium chloride independent solution 0.01Ns or less -- it is -- a room temperature (25 degrees C) -- the re-ion exchange was carried out for 1 hour, and the rate of lithium exchange was made into 87%
[0080] It dried at 40 degrees C after washing with pure water like the example overnight, and the crystalline zeolite X which carried out the re-ion exchange was activated by the 350-degree C vacua for 1 hour. The pressure at the time of activation was performed by 5 or less torrs.
[0081] a result -- an example -- the same -- Table 1 and Table 2 -- and although shown drawing 3 -6, only the low performance was obtained compared with the method of this invention
[0082] Actual PSA operation was performed using the adsorbent which carried out the ion exchange so that it might become composition of the examples 1-4 of comparison using the same molding object as

five to example of comparison 8 example. PSA operation was performed on the same equipment as an example, and conditions. The result was shown in Table 3 and Table 4.
[0083] In the adsorbent of the example of comparison, only the inferior result was obtained in the amount of oxygen, and recovery.
[0084]
[Effect of the Invention] Since the adsorbent of this invention has much content of the lithium cation located in the site (site III) which has the adsorption capacity of nitrogen with it, it has the cost performance which was excellent as an adsorbent used in order to obtain oxygen gas by the pressure rocking adsorption process (the PSA method). [there is little content of the lithium cation located in the site (Site I, site II) which is not helpful to the selective adsorption of nitrogen in the crystalline zeolite X, and high]

[Translation done.]

CLAIMS

[Claim(s)]
[Claim 1] crystalline zeolite X which has from 3.0 SiO2 / aluminum2O3 mole ratio which is not size -- it is -- in addition -- and the crystalline zeolite X adsorbent one of whose cations and/or these mixed cations of a caesium cation, a rubidium cation, a potassium cation, a thallium cation, and a silver cation the lithium cations which are meeting per AlO2 tetrahedron are less than 88% 80% or more of all cations, and are less than 5% more than per %
[Claim 2] a crystalline zeolite X adsorbent according to claim 1 -- setting -- cation-exchange site III of crystalline zeolite X I whose located lithium cations are less than 20% 10% or more of all cations -- crystalline zeolite X adsorbent characterized by things
[Claim 3] After carrying out the ion exchange of the 90% or more of the thione which is meeting per AlO2 tetrahedron of crystalline zeolite X which has from 3.0 SiO2 / aluminum2O3 mole ratio which is not size by the lithium cation, A sodium cation is made into an indispensable cation. A caesium cation, a rubidium cation, The re-ion exchange is carried out in the mixed-salt aqueous solution containing one of the monovalent cations and/or these mixed cations of a potassium cation, a thallium cation, and a silver cation. How to manufacture the claim 1 characterized by washing, drying and activating after making into less than 88% the lithium cation which is meeting per AlO2 tetrahedron 80% or more, and a crystalline zeolite X adsorbent according to claim 2.
[Claim 4] The manufacturing method of the crystalline zeolite X adsorbent which the total cation concentration of the concerned mixed-salt aqueous solution is less than [0.1N], carries out the re-ion exchange in temperature of 60 degrees C or less, and less than 5 hours, and is characterized by washing, drying and activating in the manufacture technique of a crystalline zeolite X adsorbent according to claim 3 after making into less than 88% the lithium cation which is meeting per AlO2 tetrahedron 80% or more.
[Claim 5] The air-separation technique by pressure titubation adsorption which the nitrogen in air is made to stick to this adsorbent alternatively, and carries out separation recovery of the oxygen using a crystalline zeolite X adsorbent according to claim 1 or 2.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the adsorbent used in order to carry out separation recovery of the oxygen from air by pressure titubation adsorption (called PSA Pressure Swing Adsorption for short), its process, and the air-separation method using it.
[0002] Also in industrial gas, oxygen gas is one of the most important gas and is widely used focusing on iron manufacture, pulp bleaching, etc.

[0003] If it continues till recent years, in fields, such as dust incineration and glass melting, oxygen-enrichment combustion is beginning to adopt for the purpose of NOx occurrence reduction, and the importance of oxygen gas is increasing increasingly also from the position of earth-environment protection.
[0004] Although the PSA method, the layer dissociating method, a low temperature processing, etc. are in the manufacture technique of oxygen gas, recently, the proportion of the PSA method high-concentration oxygen gas is obtained by the low cost is increasing every year.
[0005]
[Description of the Prior Art] The zeolite adsorbent which adsorbs nitrogen gas alternatively was used for the oxygen gas manufacture by the PSA method, and the adsorbent of crystalline zeolite X which mainly carried out the ion exchange by the calcium cation, or A has been used for it until now.
[0006] It has become well-known that crystalline zeolite X which carried out the ion exchange by the lithium cation in U.S. JP,3140933,B is excellent in the separation property of air on the other hand, and the adsorbent of lithium exchange crystallinity zeolite X is recently improved. In U.S. JP,3140933,B, it is shown that crystalline zeolite X is so highly efficient that the rate of lithium exchange is high, and the fact is reconfirmed in Japanese Patent Publication No. 25527 { five to }, and U.S. JP,5268023,B.
[0007] Lithium exchange crystallinity zeolite X is obtained by carrying out the ion exchange of the crystalline zeolite X using the aqueous solution containing lithium salt. However, since the lithium which is a rare metal was expensive, the crystalline zeolite X adsorbent with the high rate of lithium exchange became very expensive.
[0008] On the other hand, in addition to the lithium cation, 15% - 30% of an alkaline-earth cation is mixed substantially, and the mixed cation-exchange zeolite X adsorbent which reduced the proportion of an expensive lithium cation is also proposed 5% or more (others [No. / 5152813 / U.S. JP,5174979,B and]).
[0009] However, the coadsorption of oxygen was also large, and since the selective-adsorption nature of nitrogen was low as a result, the performance as an adsorbent for air separations was inadequate [crystalline zeolite X containing 5% or more of an alkaline-earth cation / the coadsorption], although the amount of adsorption of nitrogen was large.
[0010]
[Problem(s) to be Solved by the Invention] Although the crystalline zeolite X adsorbent which carried out the ion exchange by the lithium cation had the outstanding selective-adsorption property of nitrogen, it had become what has it in the adsorbent with the high rate of lithium exchange. [remarkable the oxygen gas cost manufactured using an adsorbent cost and such an adsorbent and high]
[0011] then, the content of an expensive lithium -- as much as possible -- low -- stopping -- in addition -- and the development of the adsorbent excellent in the cost performance which is excellent in the selective-adsorption nature of nitrogen was desired strongly
[0012]
[Means for Solving the Problem] As a result of a lithium cation's examining in detail the crystalline zeolite X adsorbent which carried out the ion exchange, even if a lithium cation is less than 88%, this invention person etc. A high air-separation performance is obtained by carrying out th ion exchange in the mixed monovalent cation aqueous solution which has a difference in the free energy in the ion exchange. Site III which is an ion-exchange site which carries out a role important for adsorption of nitrogen by carrying out the ion exchange especially of the crystallin zeolite X until a lithium cation becomes 90% or more by the meeting proportion of AlO2 tetrahedron unit first After introducing a lithium cation, A sodium cation is made into an indispensable cation. A caesium cation, a rubidium cation, By re-exchanging in the mixed-salt aqueous solution containing one of the monovalent cations and/or these mixed cations of a potassium cation, a thallium cation, and a silver cation It finds out that the performance which was excellent especially by sampling site I which is the ion-exchange site which does not participate in a nitrogen adsorption capacity, and the lithium cation of a site II is obtained, and comes to complete this invention. It is possible for the adsorbent of this invention to have few contents of an expensive lithium, to end, and to offer a highly efficient adsorbent more cheaply.
[0013] Below, this invention is explained in detail.
[0014] The mother zeolite crystal of the adsorbent used by this invention is crystalline zeolite X which has SiO2 / aluminum2O3 mole ratio which is not size, and it is especially more desirable than 3.0 that SiO2 / aluminum2O3 mole ratio is crystalline zeolite X of 1.8-2.5.
[0015] Crystalline zeolite X is classified into a ********** site type (it is written as a henceforth FAU type) in crystallography, and is expressed with the following chemical formulas.
[0016] Mn O, aluminum2 O3, mSiO2, and lH2 O (the cation of m=2-3 and M:2/n **, l=0-8)
Why the zeolite kind of an adsorbent must be crystalline zeolite X here is explained.
[0017] electrostatic [according / adsorption of the nitrogen to a zeolite and oxygen is physical adsorption, and / especially to the polarity (quadrupole child) of nitrogen and oxygen] -- **** adsorption is the main adsorption driving force since nitrogen has the high quadrupole child moment compared with oxygen -- the adsorption to a zeolite -- electrostatic -- if it is only **** attractive force, high selectivity is obtained compared with oxygen adsorption, and nitrogen adsorption can expect a high value to the selectivity (it is expressed as a separation factor here) of the nitrogen defined as relative volatility, and oxygen
[0018] On the other hand, nitrogen and oxygen are adsorbed by dispersion force (intermolecular force) to a zeolite. Since adsorption by dispersion force does not have the selectivity of nitrogen adsorption and oxygen adsorption regardless of the polarity of an admolecule, a

separation factor approaches 1. Since di on force is th interaction of a zeolite crystal and olecule, in th parvus, th influence of dispersion force becomes [the adsorpti e in a zeolite] larg , and the selectivity of nitrogen adsorption and oxygen adsorption falls.
[0019] Ther for , in order to rais the selectivity of nitrog n adsorption, the adsorption space of the mother zeolite crystal must b large, and it is the zeolit kind with which crystalline zeolite X with large pore was most suitable for the air separation.
[0020] On the other hand, it is known that crystallin zeolite Y also belongs to the FAU same in crystallography as crystalline zeolite X. How v r, crystalline zeolite Y is the ion-exchange site III important for nitrogen adsorption. Since a lithium cation has th specific property in which it is not xchanged, it cannot use for the mother zeolite of this invention.
[0021] Next, the mother zeolite crystal of the adsorbent used by this inv ntion explains the ground which must be crystallin zeolite X which has from 3.0 SiO2 / aluminum2O3 mole ratio which is not size.
[0022] Or more by three, SiO2 / aluminum2O3 mole ratio cannot serve as Y, and cannot use a zeolite for the ground described previously.
[0023] Since the electrostatic attraction of a zeolite is formed of the exchange cation of a zeolite, more ones are [the number of cations] desirable. Although the amount of charge divalence may exist to AlO2 tetrahedron of a zeolite, in the zeolite with AlO2 higher proportion per unit weight, i.e., the parvus zeolite of SiO2 / aluminum2O3 ratio, the adsorption site of the cation of a zeolite increases.
[0024] Although, as for crystalline zeolite X, SiO2 / aluminum2O3 mole ratio can take less than three, especially in this invention, a high performance is obtained for SiO2 / aluminum2O3 mole ratio in parvus 1.8-2.5.
[0025] The mother zeolite crystal of the adsorbent of the above ground to this invention has a large micropore under crystal, and it is especially desirable that it is [whose parvus crystallinity zeolite X of SiO2 / aluminum2O3 ratio, i.e., SiO2 / aluminum2O3 mole ratio, is not size from 3] crystalline zeolite X of 1.8-2.5.
[0026] Next, the rate of the ion exchange of the adsorbent of this invention is explained.
[0027] As for the proportion of a lithium cation, it is desirable that the lithium cations to which the adsorbent of this invention is meeting per AlO2 tetrahedron are less than 88% 80% or more of all cations, and are especially less than 88% 85% or more.
[0028] Since the lithium is especially expensive at 90% or more and the final rate of lithium exchange of this invention becomes [an adsorbent cost] high 88% or more, it is not desirable. On the other hand, the rate of lithium exchange is the target ion-exchange site III at less than 80%. Since sufficient lithium cation cannot remain, it is not desirable.
[0029] Although the adsorbent of this invention contains one of the monovalent cations and/or these mixed cations of a caesium cation, a rubidium cation, a potassium cation, a thallium cation, and a silver cation as cations other than a lithium, especially the content of these monovalent cations has 2 to 4% of a desirable domain less than 5% more than per %. The content of these monovalent cations is a site III at 5% or more. Li cannot be maintained 10% or more, but an air-separation property decreases remarkably. A cation's presence position (site) is explained in full detail behind. Cations other than a lithium cation and these monovalent cations are sodium cations.
[0030] The adsorbent of this invention is the cation-exchange site III of a crystalline X type zeolite. The located lithium cation is less than 20% 10% or more.
[0031] It is known well that three ion-exchange sites (site I, site II, and the site III are called) exist in crystalline zeolite X. The site position of crystalline zeolite X was shown in drawing 1 .
[0032] The cation located in an ion-exchange site forms an electrostatic field around the, and adsorbs a polar substance. Site III Since the located lithium cation exists in a crystal front face naked and can form a strong electrostatic field, it is a site convenient for nitrogen adsorption.
[0033] With the conventional ion-exchange technique, a lithium cation will be altogether located in site I and the site II whose lithium cation is a stable site thermodynamically in less than 80% of all cations. Therefore, at 80% or less, a nitrogen adsorption capacity has a low rate of lithium exchange, and, for the rate of exchange, a lithium cation is a site III for the first time at 80% or more. It was located, and nitrogen adsorptivity ability was improving as the rate of exchange became high.
[0034] With the adsorbent of this invention, although the rate of a lithium cation exchange is low, it is the exchange site III of zeolite X. By making the existing effective lithium cation into 10% or more, the selective-adsorption performance of nitrogen equivalent to the case where the rate of exchange is 90% or more can be demonstrated. On the other hand, it is the site III of crystalline zeolite X. The cation which may exist is to 20% of all cations, and it is a site III about 20% or more of a lithium cation. It is impossible for you to make it located.
[0035] It can ask for the proportion of the lithium cation of crystalline zeolite X correctly by chemical analyses (ICP etc.). Ion-exchange site III Although it can ask for the proportion of the existing lithium cation also in an X ray crystal structure analysis or neutron-beam analysis, it can be estimated from the adsorption property of nitrogen simpler.
[0036] For lithium exchange crystallinity zeolite X by the conventional ion-exchange method, the rate of a lithium cation exchange is 80% to the exchange site III. Since it begins to be located, the rate of lithium exchange is a site III at 80% or more of crystalline zeolite X. The lithium cation and nitrogen adsorptivity ability which are located are in a proportionality, and it is the rate of lithium exchange and the site III of crystalline zeolite X. The proportion of the existing lithium can be estimated from a nitrogen adsorption property (a nitrogen
[0037] Next, the manufacture technique of the crystalline zeolite X adsorbent of this invention is explained.
[0038] Although the mother zeolite crystal used by this invention is crystalline zeolite X which has from 3.0 SiO2 / aluminum2O3 mole ratio which is not size, especially the manufacture technique of crystalline zeolite X is not limited, but can be compounded by well-known technique. For example, as for the manufacture technique of parvus crystallinity zeolite X, SiO2 / aluminum2O3 mole ratio is indicated by U.S. JP,2882244,B etc.
[0039] Although the adsorbent of this invention may also contain a binder, what zeolite-ized the binder component (binder loess) may be used. A binder kind is not limited but can illustrate a silica binder, an alumina binder, an aluminum-silicate binder, a clay binder, etc. Since a binder does not have adsorptivity ability, the proportion of a binder has a few desirable thing.
[0040] The size of the adsorbent of this invention and a configuration are not limited, either, for example, the bead configuration and the pellet configuration where a path is 1.0-2.0mm can be illustrated.
[0041] The ion exchange of the above-mentioned crystalline zeolite X is carried out 90% or more by the lithium cation, and the adsorbent of this invention is III of the ion-exchange site of crystalline zeolite X. It is desirable to fully exchange a lithium cation. As for especially the rate of exchange of the lithium cation in this phase, it is desirable that all cations are 95% to 100% 90% or more.
[0042] Although especially the ion-exchange technique is not limited, the technique of making the lithium salt aqueous solution (for example, lithium-chloride aqueous solution) which adjusted crystalline zeolite X to pH 10-11 by the lithium hydroxide, for example contacting can be illustrated. Although a batch type or a circulation formula is sufficient as the ion exchange, the ion exchange of a circulation formula is efficient. Although especially the temperature of the ion exchange is not limited, either, the higher one of temperature is especially efficient and it is desirable to carry out at 60 degrees C - 90 degrees C 40 degrees C - 100 degrees C.
[0043] By this invention, the re-ion exchange of exchang site I which does not participate in adsorption of nitrogen, and the lithium cation of a site II is carried out by other cations from crystalline zeolite X which fully carried out the ion exchange by the lithium cation.
[0044] A part of rank of the free energy of a cation exchange was illustrated to drawing 2 . Since the status of the sodium cation which is a start raw material served as criteria, the energy level of a sodium type zeolite was set to 0.
[0045] As shown in this drawing 2 , **G to the caesium cation from a sodium cation, a rubidium cation, a potassium cation, a thallium cation,

and a silver cation which carries out the [illegible]change is a negative value, and a reaction tends [illegible]ress.

[0046] On the other hand, **G of the ion [illegible]nge from a sodium cation to a lithium cation is a positiv value, a reaction seldom happens, and **G of the ion exchange is site I, site II, and the site III further. It becomes large and is hard to xchange in order in th order of site III > site II> site I. In the ion xchange in a lithium, it is asked for **G being larg from an ion-exchange-equilibrium constant in the order of site III > sit II> site I.

[0047] By this invention, th re-ion exchange of exchange site I which does not participate in adsorption of nitrogen, and the lithium cation of a site II is carried out by other cations from crystallin zeolite X which fully carried out the ion exchang by the lithium cation. However, it is a site III if crystallin zeolite X which carried out the ion exchange by the lithium cation is re-exchanged with sodium cation independent ion- xchange liquid. Site III which is a cation important for nitrogen adsorption since xchange of a lithium cation has negative biggest **G The ion xchange of the lithium cation will be carried out preferentially.

[0048] this invention person etc. here A sodium cation, a caesium cation, a rubidium cation, A potassium cation, a thallium cation, It sets to re-exchange of the mixed ion-exchange solution containing one of the monovalent cations and/or these mixed cations of a silver cation, and is a site III. Site I and the lithium cation of a site II rather than the ion exchange of the lithium cation is carried out to a sodium cation Caesium cation, The direction of **G which carries out the ion exchange to the monovalent cation of a rubidium cation, a potassium cation, a thallium cation, or a silver cation finds out a large thing. A sodium cation, a caesium cation, a rubidium cation, a potassium cation, In the re-ion exchange of the mixed-salt system of the cation containing one of the monovalent cations and/or these mixed cations of a thallium cation and a silver cation, it found out that site I and the lithium cation of a site II could be sampled.

[0049] The ion-exchange solution used for the re-ion exchange by this invention must contain both the monovalent cations of a sodium cation, a caesium cation and a rubidium cation, a potassium cation, a thallium cation, or a silver cation, and/or these mixed cations.

[0050] The amount of the monovalent cations of a caesium cation, a rubidium cation, a potassium cation, a thallium cation, or a silver cation and/or these mixed cations used must be less than 5% of all the exchange cations of crystalline zeolite X after carrying out the re-ion exchange, and 2 to 4% of its domain is especially desirable. The selective-adsorption performance of nitrogen is spoiled for these monovalent cations by 5% or more of all the exchange cations of crystalline zeolite X.

[0051] The concentration of the ion-exchange liquid which carries out the re-ion exchange in the ion exchange of this invention is less than 0.1N], and it is desirable that it is especially less than [0.01N]. the ionic strength of re-ion-exchange liquid -- being strong (that is, concentration being high) -- large site III of **G Since the reaction from which a lithium cation escapes becomes easy to advance, it is not desirable.

[0052] Moreover, what is necessary is just to also carry out re-ion-exchange temperature at a room temperature (25 degrees C) for the lower one to be desirable from the ground same as the above, it be desirable to carry out below 60 degrees C, and for it be convenient.

[0053] Moreover, re-ion-exchange time has the shorter desirable one. If a re-swap time is long, an ion-exchange site shifts to the status stabl in energy, and it is a site III. A lithium cation will re-exchange for site I and the site II. Especially re-ion-exchange time has less than 2 desirable hours less than 5 hours.

[0054] By the ion exchange treatment of the adsorbent of this invention, separation recovery of the lithium collected from site I and the site II is carried out with the ion exchange, chemistry settling, etc., and it can be reused effectively. recovery of a lithium cation, and the reuse technique -- various kinds -- the technique is not limited although well-known technique is applicable

[0055] Next, after the above-mentioned ion exchange, the adsorbent of this invention performs washing, xeransis, and heat treatment (activation), and they are used for it as a target adsorbent for the first time.

[0056] Although washing, xeransis, and especially activation conditions are not limited, it can illustrate that washing uses a pure water or the water which adjusted pH to weak alkali by the lithium hydroxide of a minute amount.

[0057] It is desirable that performing xeransis at low temperature performs 100 degrees C at 30 degrees C - 60 degrees C especially from a room temperature preferably.

[0058] It is desirable to perform it in the status that a low-temperature steam partial pressure is low if possible, although an activation is processing which removes the moisture which is sticking to crystalline zeolite X by heating. For example, heat treatment of the inner heat type which supplies the vacuum heat-treatment in 300 degrees C - 600 degrees C, heated air, pure nitrogen or pure oxygen of a low dew-point among a vacuum can be illustrated.

[0059] Since the lithium cation to which the crystalline zeolite X adsorbent of this invention is meeting to AlO_2 tetrahedron is less than 88%, the lithium cation which is meeting to AlO_2 tetrahedron proposed previously differs from 88% or more of an adsorbent (U.S. JP,4859217,B, Japanese Patent Publication No. 5-25527).

[0060] The alkaline-earth-metal cation by which the conventional proposal of the crystalline zeolite X adsorbent of this invention was made, not using an alkaline-earth-metal cation at all completely differs from 5% or more of a crystalline zeolite X adsorbent (others [No. / 5152813 / U.S. JP,5174979,B and]).

[0061] Since elements other than a lithium are monovalent cations, the crystalline zeolite X adsorbent of this invention differs from the previous r port patent (Japanese Patent Publication No. 4707 [eight to], publication number 256094 [seven to]) which has proposed adding a bivalent or trivalent cation.

[0062] For the total rate of exchange of a lithium cation, the adsorbent of this invention is a site III with the technique of U.S. JP,5268023,B, although U.S. JP,5268023,B is overlapped. Since it can enter only to 8% by the maximum, a lithium cation is a site III. As for the adsorbent of 10% or more of this invention, a lithium cation differs from the adsorbent of U.S. JP,5268023,B.

[0063] Since the adsorbent of this invention has the outstanding selective-adsorption ability of nitrogen, it makes nitrogen adsorb alternatively from air, and has the performance which was extremely excellent as an adsorbent used for the pressure titubation adsorption process (th PSA m thod) which obtains oxygen gas as a product.

[0064] The pressure titubation adsorption process (the PSA method) said by this invention makes the nitrogen in air adsorb alternatively, fluctuating a pressure, if it is the oxygen PSA method for obtaining oxygen gas as a product, there is especially no limitation in the service condition, 3, the PSA method of 2 column type, the VSA method, the VPSA method, etc. do not depend on the operation pressure range of titubation adsorption from 4 column type, but a high performance can be demonstrated.

[0065]

[Example] Next, although a concrete example explains this invention, this invention is not limited to these examples.

[0066] First, using the lithium chloride (it adjusts to pH-11 by the lithium hydroxide) of 1N, the rate of lithium exchange was made into 95%, and the pure water washed the example 1 - 10 crystallinity zeolite X. next, salt concentration -- the sodium not more than 0.01N, a rubidium, caesium and a thallium, silver, and the mixed-salt ghost aqueous solution of a potassium -- using -- a room temperature (25 degrees C) -- the re-ion xchange was carried out for 1 hour It dried at 40 degrees C after washing with the pur water ov rnight, and crystalline zeolite X which carried out the re-ion exchange was activated by the 350-degree C vacua for 1 hour. The pressure at the time of an activation was performed by 5 or less torrs.

[0067] The separation factor (alpha) of the air in SiO_2 / aluminum2O3 mol ratio of crystalline zeolit X which is the mother zeolite

(Si/aluminum2), Li / aluminum ratio, the r[redacted]a cation xchange, the nitrogen amount of adsor[redacted]N2) in 700torr, and nitrogen partial pressure 700torr was shown in Tabl 1, [redacted]2, and the drawings 3 -6.

[0068]

[Table 1]

No.	Si/Al2	Li/Al	カチオン交換率 (%)							サイトIII Liカチオン率 (%)	QN2 (Ncc/g) at 10℃	α
			Li	Tl	Rb	Cs	Ag	K	Na			
実施例1	2.5	86	88	3	-	-	-	-	9	13±1	25.5	4.7±0.1
実施例2	2.5	86	88	-	2	-	-	-	10	13±1	25.3	4.6±0.1
実施例3	2.5	85	87	-	-	2	-	-	11	13±1	25.7	4.5±0.1
実施例4	2.5	85	87	-	-	-	3	-	10	13±1	24.8	4.6±0.1
実施例5	2.5	86	87	-	-	-	-	3	10	13±1	24.7	4.6±0.1
比較例1	2.5	86	87	-	-	-	-	-	13	7±1	19.0	4.1±0.1
比較例2	2.5	86	87	-	-	-	-	-	13	7±1	19.5	4.2±0.1

[0069]

[Table 2]

No.	Si/Al2	Li/Al	カチオン交換率 (%)							サイトIII Liカチオン率 (%)	QN2 (Ncc/g) at 10℃	α
			Li	Tl	Rb	Cs	Ag	K	Na			
実施例 6	2.0	86	88	2	-	-	-	-	9	13±1	27.5	5.7±0.1
実施例 7	2.0	86	88	-	2	-	-	-	10	13±1	27.3	5.8±0.1
実施例 8	2.0	85	87	-	-	2	-	-	11	13±1	27.0	5.5±0.1
実施例 9	2.0	85	87	-	-	-	2	-	10	13±1	27.8	5.6±0.1
実施例10	2.0	86	87	-	-	-	-	3	10	13±1	27.4	5.6±0.1
比較例3	2.0	86	87	-	-	-	-	-	13	7±1	20.5	5.0±0.1
比較例4	2.0	86	87	-	-	-	-	-	13	7±1	21.0	5.1±0.1

[0070] The nitrogen partial pressure computed the separation factor (alpha:relative volatility) of the air in 700torrs by several 1 of the following.

[0071]

[Equation 1]

$$\text{分離係数} = \frac{\text{窒素吸着量 (at 700torr)}}{\text{酸素吸着量 (at 700torr)}} \times \frac{\text{空気中の酸素濃度}}{\text{空気中の窒素濃度}}$$

[0072] The performance of Li exchange zeolite obtained with the conventional technique was also collectively shown in drawings 3 -6. By th technique of this invention, the nitrogen amount of adsorption with the rate higher than the case where the conventional technique is used on the base of 80% of a lithium cation exchange, and the separation factor were obtained.

[0073] 90% of the weight, as a binder, the granulation of the molding field of example 11, - 20 crystallinity zeolite x diameter [which consists of 10 % of the weight of kaolin binders / of 1.5mm] phi was carried out, and actual PSA operation was performed using the adsorbent which carried out the ion exchange so that it might become composition of examples 1-10.

[0074] PSA operation was made into 2 column type which an adsorption tower with a capacity of 2l. becomes from two, and the adsorption cycle was made into double ** 30 seconds for desorption 30 seconds for adsorption 1 minute. The pressure swing domain was set to adsorptive pressure force 890torr (nitrogen partial pressure 700torr) and desorption pressure 180torr, and temperature of an adsorption tower was performed by two points, 0 degree C and 10 degrees C.

[0075] The result was shown in Table 3 and 4.

[0076]

[Table 3]

ＰＳＡ評価結果（ＳＩ／ＡＩ：[illegible]５）

Ｎｏ．	組成	温度（℃）	酸素量（NL/kgh）	回収率（％）
実施例１１	実施例１と同等	0	82.0	57.0
		10	74.0	58.5
実施例１２	実施例２と同等	0	80.5	56.5
		10	72.5	57.5
実施例１３	実施例３と同等	0	82.5	56.0
		10	74.5	57.0
実施例１４	実施例４と同等	0	82.0	57.5
		10	74.0	56.5
実施例１５	実施例１と同６	0	82.5	57.5
		10	74.0	57.0
比較例５	比較例１と同等	0	75.0	50.5
		10	70.0	51.0
比較例６	比較例２と同等	0	76.5	51.0
		10	71.0	51.5

[0077]
[Table 4]

ＰＳＡ評価結果（Ｓｉ／Ａｌ₂ [illegible] ０）

Ｎｏ．	組成	温度（℃）	酸素量（NL/kgh）	回収率（%）
実施例１６	実施例６と同等	0	106.5	65.0
		10	95.0	63.5
実施例１７	実施例７と同等	0	104.0	63.0
		10	93.5	62.0
実施例１８	実施例８と同等	0	106.0	64.0
		10	92.0	61.5
実施例１９	実施例９と同等	0	105.5	63.5
		10	93.0	61.5
実施例２０	実施例１０と同等	0	105.0	63.5
		10	92.5	61.0
比較例７	比較例３と同等	0	99.0	53.5
		10	88.0	53.0
比較例８	比較例４と同等	0	100.0	54.0
		10	90.0	53.5

[0078] The adsorbent of this invention shows a high performance also in actual PSA operation, and the high performance was demonstrated also in the low-temperature property (0 degree C) which poses a problem especially in a real plant.
[0079] The rate of lithium exchange was first made into 87% and 95% for the example 1 of a comparison, - 4 crystallinity zeolite X using the lithium chloride (it adjusts to pH-11 by the lithium hydroxide) of 1N. the Plastic solid of 95% of the rates of lithium exchange -- salt concentration -- the sodium chloride independent aqueous solution not more than 0.01N -- it is -- a room temperature (25 degrees C) -- the re-ion exchange was carried out for 1 hour, and the rate of lithium exchange was made into 87%
[0080] It dried at 40 degrees C after washing with the pure water like the example overnight, and crystalline zeolite X which carried out the re-ion exchange was activated by the 350-degree C vacua for 1 hour. The pressure at the time of an activation was performed by 5 or less torrs.
[0081] a result -- an example -- the same -- Table 1 and Table 2 -- and although shown drawing 3 -6, only the low performance was obtained compared with the technique of this invention
[0082] Actual PSA operation was performed using the adsorbent which carried out the ion exchange so that it might become composition of the examples 1-4 of a comparison using the same molding field as five to example of comparison 8 example. PSA operation was performed on the same equipment as an example, and conditions. The result was shown in Table 3 and Table 4.
[0083] In the adsorbent of the example of a comparison, only the inferior result was obtained in the amount of oxygen, and recovery.
[0084]
[Effect of the Invention] Since the adsorbent of this invention has much content of the lithium cation located in the site (site III) which has th adsorption capacity of the nitrogen with it, it has the cost performance which was excellent as an adsorbent used in order to obtain oxyg n gas by the pressure titubation adsorption process (the PSA method). [there is little content of the lithium cation located in the site (site I, site II) which is not helpful to the selective adsorption of nitrogen in crystalline zeolite X and high]

[Translation done.]